PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-195518
(43)Date of publication of application : 14.07.2000

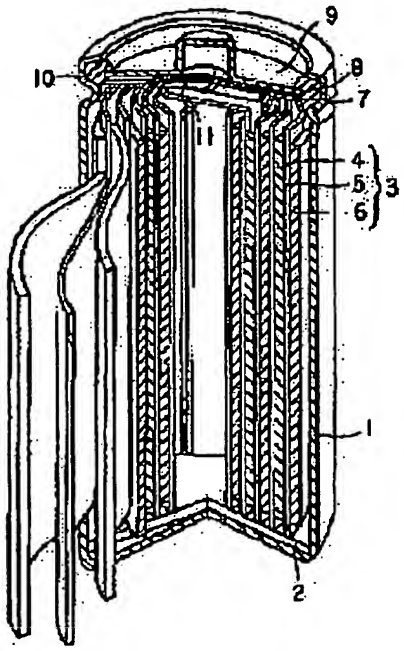
(51)Int.Cl. H01M 4/62
H01M 4/02
H01M 10/40

(21)Application number : 10-372466
(22)Date of filing : 28.12.1998

(71)Applicant : TOSHIBA CORP
(72)Inventor : SAKURAI KATSUYUKI
ISOZAKI YOSHIYUKI
HASEBE HIROYUKI

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery that is excellent in adhesion between a collector and an active material layer and also excellent in a cycle life characteristic.
SOLUTION: In relation to a nonaqueous electrolyte secondary battery provided with, as battery element parts, a positive electrode 4 composed by supporting a mixture of a positive electrode active material and a binder on a collector, a negative electrode 6 composed by supporting a mixture of a negative electrode active material and a binder on a collector, and a nonaqueous electrolyte, the feature of this battery is that the carbon material of the negative electrode active material constituting the negative electrode 6 is formed of a mixture of a carbon fiber material (A) and a carbonaceous material (B), and the negative electrode binder contains at least an acrylic rubbery copolymer.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] In the nonaqueous electrolyte rechargeable battery which possesses the positive electrode which makes a charge collector come to support the mixture of positive active material and a binder, the negative electrode which makes a charge collector come to support the mixture of a negative-electrode active material and a binder, and nonaqueous electrolyte as the cell element section The nonaqueous electrolyte rechargeable battery characterized by for the carbon material of the negative-electrode active material which constitutes a negative electrode consisting of mixture of a carbon fiber ingredient (A) and a carbonaceous ingredient (B), and said negative-electrode binder containing an acrylic gum copolymer at least.
[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by this vinylidene fluoride system copolymer being 50 or less % of the weight by this negative-electrode binder consisting of mixture of an acrylic gum copolymer and a vinylidene fluoride system copolymer.
[Claim 3] Claim 1 characterized by a carbonaceous ingredient (B) being 50 or less % of the weight among the mixture of the carbon fiber ingredient (A) of this negative-electrode active material carbon material, and a carbonaceous ingredient (B) thru/or a nonaqueous electrolyte rechargeable battery according to claim 2.
[Claim 4] Claim 1 characterized by being three or more active material pack density 1.3 g/cm of this negative electrode thru/or a nonaqueous electrolyte rechargeable battery according to claim 2.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery using especially the carbonaceous ingredient as a negative-electrode active material with respect to the nonaqueous electrolyte rechargeable battery which uses the organic electrolytic solution.
[0002]
[Description of the Prior Art] In recent years, high capacity-ization to the rechargeable battery which is the power source of these electronic equipment is demanded with the miniaturization of electronic equipment, such as a cellular phone and VTR, and buildup of need. Moreover, the air pollution by the exhaust gas from an automobile serves as a social problem, and using a rechargeable battery lightweight as a power source for electric vehicles and highly efficient is expected.
[0003] As this rechargeable battery, the nonaqueous electrolyte rechargeable battery which combined LiCoO2 positive electrode with the carbon negative electrode is developed, and it is used for the current large quantity.
[0004] In order to realize the non-aqueous-solvent rechargeable battery of high capacity, high-capacity-izing of an active material and the formation of high density restoration of an electrode are required.
[0005] The electrode for said non-aqueous-solvent rechargeable batteries is produced, when the slurry obtained by adding an active material to the solution which made the organic solvent distribute a binder, and carrying out distributed mixing is rolled out after spreading and desiccation and carries out the shape of sheet metal on a charge collector.
[0006] In the configuration of the above-mentioned electrode, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), an ethylene-propylene-diene copolymer (EPDM), a styrene butadiene rubber (SBR), etc. can be used as a binder, for example. Among these binders, a polyvinylidene fluoride fluororesin has the solubility-proof over a certain amount of electrolytic solution, solution retention and ion conductivity, and the resistance to the active species produced by electrode reaction, and is widely used as a binder of said electrode for non-aqueous-solvent rechargeable batteries.
[0007] However, when fluororesins, such as polyvinylidene fluoride, are used, the electrode which is produced in the case of a negative electrode is comparatively hard, and since the adhesive property of an active material layer and a charge collector is not enough, it is easy to produce the crack at the time of cell winding, omission of an active material, etc. in the configuration of the above-mentioned electrode. Crack generating, omission of an active material, etc. not only serve as trouble, such as improvement in a cell energy density, but Although the thing whose adhesive property of an active material layer and a charge collector is imperfection among the . aforementioned explanation leading to cycle lowering [**** / raising the probability of inter-electrode short generating] of a cell is the case where PVDF is a comparatively small addition Although the adhesive property with a charge collector will improve for the densification of an electrode, and high capacity-ization if the rate of closing to the electrode of the addition of PVDF makes [many] an addition to some extent when the fewer possible one is good ., i.e., PVDF An electrode becomes hard, and the rate of occupying to an electrode increases, and it is a

problem at the densification of an electrode, and high capacity-ization.
[0008] Fluororesins, such as a copolymer which furthermore makes basic structure the above-mentioned polyvinylidene fluoride and vinylidene fluoride, have a problem in manufacture of an electrode, a work environment cost side, etc.
[0009]
[Problem(s) to be Solved by the Invention] In the configuration of the above-mentioned negative electrode, if fluororesins, such as polyvinylidene fluoride, are used as a binder and the addition of said binder is lessened for the purpose of high-capacity-izing and densification, an electrode is hard, and when winding etc. is carried out, it will be easy to produce a crack, and will be easy to cause omission of an active material etc. with the not sufficient adhesive property of a negative-electrode active material layer and a charge collector. Exfoliation of the active material layer of this electrode, elopement, a crack, etc. not only serve as trouble, such as improvement in a cell energy density, but will raise the probability of inter-electrode short generating, or the cycle-life property of a cell will fall.
[0010] This invention coped with the above-mentioned situation, was made, and aims at offering the nonaqueous electrolyte rechargeable battery excellent in the cycle-life property.
[0011]
[Means for Solving the Problem] In the nonaqueous electrolyte rechargeable battery which possesses the positive electrode which makes a charge collector come to support the mixture of positive active material and a binder, the negative electrode which makes a charge collector come to support the mixture of a negative-electrode active material and a binder, and nonaqueous electrolyte as the cell element section, the carbon material of the negative-electrode active material which constitutes a negative electrode consists of mixture of a carbon fiber ingredient (A) and a carbonaceous ingredient (B), and said negative-electrode binder is the nonaqueous electrolyte rechargeable battery characterized by being an acrylic copolymer.
[0012] the time of . carbon fiber ingredient (A) based on the following reason being used for having specified the carbon material of said negative-electrode active material as the mixture of a carbon fiber ingredient (A) and a carbonaceous ingredient (B) -- since the electric conduction network between active materials is not enough -- a carbonaceous ingredient (B) -- the clearance between carbon fiber ingredients (A) -- burying -- the macro between carbon fiber ingredients ---like -- electric conduction network formation is carried out. Moreover, . which can aim at a capacity rise, and high pack density-ization of an electrode can also be achieved by paying carbonaceous ingredients (B) to the clearance between carbon fiber ingredients (A).
[0013] Moreover, when a carbonaceous ingredient (B) goes into the clearance between carbon fiber ingredients (A), the binding property between carbon fiber ingredients (A) can be raised.
[0014] That is, by adding a carbonaceous ingredient (B), the conductivity between carbon fiber ingredients (A), contact nature, etc. can improve, and high-capacity-izing, densification, etc. can be achieved. Moreover, since the press of self-lubrication-properties, such as a carbonaceous ingredient (B), for example, graphite powder etc., to an electrode becomes easy, it becomes easy to move a carbon fiber ingredient (A) and pack density is easy to be raised by adding a carbonaceous ingredient, it becomes more desirable.
[0015] Moreover, even if the binder which consists of said acrylic copolymer is immersed in the electrolytic solution for a long period of time, it is hardly swollen, and flexibility is in an electrode, and since it excels also in adhesion with a charge collector by little addition, the lithium secondary battery excellent in the cycle-life property can be obtained by considering as the lithium secondary battery of a configuration like this invention.
[0016] As said carbon fiber ingredient (A), the average fiber length of 10-100 micrometers, . with desirable it being specific-surface-area 0.1-5m2/g in 1-20 micrometers of diameters of average fiber, and aspect ratios (a fiber length/diameter of fiber) 2-10 -- again . with desirable the peak intensity ratio (P101/P100) of the diffraction peak P101 and the diffraction (100) peak P110 by the X-ray diffraction method (101) being 1.2 or more -- further d002 more preferably 0.3354-0.3370nm 0.3354-0.3359nm, . with desirable La being 60nm or more and Lc being 40nm or more . with still more desirable the

exothermic peak by the differential thermal analysis in air being 800 degrees C or more -- for example A carbonaceous ingredient, the carbonization object of a vapor growth carbon body, etc. using a mesophase pitch based carbon fiber, a PAN system carbon fiber, phenol resin, and polyimide as carbon fiber-like powder are mentioned.

[0017] As said carbonaceous ingredient (B), a configuration is the carbon powder of the shape of a globular shape, a thin film integrated circuit, or a grain, and it is desirable that mean particle diameter is small into said carbon fiber ingredient (A). For example, the . aforementioned carbonization object or the graphitization object with desirable it being the carbonization object or graphitization object whose mean particle diameter is 5-30 micrometers That whose d002 is 0.3354nm or more and less than 0.370nm, respectively to desirable . pan . with desirable the peak intensity ratio (P101/P100) of the diffraction peak P101 and the diffraction (100) peak P110 by the X-ray diffraction method (101) being 1.2 or more -- it is still more desirable that the exothermic peak by the differential thermal analysis in air is 800 degrees C or more. For example, it is desirable that they are specifically powder, such as a mesophase microsphere, corks, a carbonization object of a vapor growth carbon body, a graphitization object, an artificial graphite, or a natural graphite.

[0018] The acrylic gum copolymer as said binder comes to carry out copolymerization of unsaturated carboxylic acid and unsaturated-carboxylic-acid alkyl ester, such as an acrylic acid and a methacrylic acid, to gum copolymers, such as an aromatic series vinyl-conjugated diene system copolymer or an ethylene nature nitryl compound-conjugated diene system copolymer, as a raw material monomer.

[0019] As other unsaturated carboxylic acid, itaconic-acid, fumaric-acid, maleic-acid, crotonic-acid, citraconic-acid, mesaconic acid, glutaconic acid, and maleic-acid mono-octyl, maleic-acid monobutyl, ITADON acid mono-octyl, etc. are mentioned. Moreover, unsaturated-carboxylic-acid anhydrides, such as an anhydrous acrylic acid, an anhydrous methacrylic acid, and a maleic anhydride, may be used.

[0020] As alkyl ester of said unsaturated carboxylic acid A methyl acrylate, an ethyl acrylate, acrylic-acid propyl, acrylic-acid isopropyl, Butyl acrylate, acrylic-acid octadecyl, acrylic-acid hydroxyethyl, Acrylic-acid propylene glycol, an acrylic-acid amide, metaglycidyl acrylate, A methyl methacrylate, ethyl methacrylate, methacrylic-acid propyl, Methacrylic-acid isopropyl, methacrylic-acid butyl, cyclohexyl methacrylate, Methacrylic-acid 2-(diethylamino) ethyl, methacrylic-acid hydroxypropyl, a meta-chestnut amide, glycidyl methacrylate, dimethylaminoethyl methacrylate, methacrylic-acid tert-butylamino ethyl, etc. are mentioned.

[0021] Said aromatic series vinyl-conjugated diene system copolymer comes to carry out copolymerization of an aromatic series vinyl compound and the conjugated diene system compound as a raw material monomer.

[0022] As this aromatic series vinyl compound, styrene, alpha methyl styrene, vinyltoluene, p-t-butyl toluene, etc. are mentioned.

[0023] A butadiene, piperylene, etc. can be mentioned as said conjugated diene system compound.

[0024] Said ethylene nature nitryl compound-conjugated diene system copolymer comes to carry out copolymerization of an ethylene nature nitryl compound and the conjugated diene system compound as a raw material monomer.

[0025] As this ethylene nature nitryl compound, acrylonitrile (meta), croton nitril, allyl compound nitril, etc. are mentioned.

[0026] Moreover, as a solvent which distributes said acrylic gum copolymer, polar solvents, such as a N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF), are used. In this case, when the polar gum copolymer to which the polarity was made to give by carrying out copolymerization of what has 2 tolyl groups to said gum copolymer is used, since it becomes easy to distribute to said polar solvent, it is desirable.

[0027] As a compound which has said nitrile group, acrylonitrile (meta), croton nitril, allyl compound nitril, etc. are mentioned.

[0028] Although the content of the acrylic copolymer as said binder is specified to 10 or less % of the weight to the weight of the mixture of the carbon fiber ingredient (A) which is a negative-electrode active material, and a carbonaceous ingredient (B), it is 5 or less % of the weight to negative-electrode

active material weight preferably.
[0029] Furthermore, said negative-electrode binder consists of mixture of an acrylic copolymer and a vinylidene fluoride system copolymer. When . negative-electrode binder with desirable a vinylidene fluoride system copolymer being 50 or less % of the weight in said binder is the mixture of an acrylic copolymer and a vinylidene fluoride system copolymer, . with the property in which an acrylic copolymer maintains the adhesive property of a charge collector and an active material, and a vinylidene fluoride system copolymer has the good solution retention of the electrolytic solution, In the . aforementioned binder which can offer the cell which was excellent in the cycle property by taking in both properties, swelling of an electrode becomes [a vinylidene fluoride system copolymer] large at 50 % of the weight or more. Since the solution retention of an electrode has . one side and the vinylidene fluoride system copolymer with which the adhesive property of an active material layer also falls, and a cycle property falls to some extent at less than 50 % of the weight and the adhesive property of an active material layer is also acquired enough, It is desirable that a carbonaceous ingredient (B) is 50 or less % of the weight among the mixture of the carbon fiber ingredient (A) of the . aforementioned negative-electrode active material carbon material excellent in the cycle property and a carbonaceous ingredient (B).
[0030] A carbonaceous ingredient (B) has 50 or less desirable % of the weight among the mixture of a carbon fiber ingredient (A) and a carbonaceous ingredient (B). If . carbonaceous ingredient (B) by which the following things are raised as a reason is ****ed to 50% of the weight or more, the property of a carbon fiber ingredient will no longer begin to be attracted fully. If it uses, a carbonaceous ingredient (B), for example, a graphite, with large . to which a rate property and a cycle property worsen and specific surface area, production of electrode paste will become very difficult and decline in a solid content ratio and consumption of the amount of binders will become remarkable. On the other hand, at less than 50 % of the weight, the property of a carbonaceous ingredient fully begins to be attracted and, as for the carbon fiber (ingredient A) independent twist, a rate property and a cycle property become good. Moreover, production of electrode paste becomes easy by ****ing to less than 50% of the weight, large carbonaceous ingredient (B), for example, graphite, of specific surface area.
[0031] It is characterized by being three or more active material pack density 1.3 g/cm of a negative electrode.
[0032] By making it three or more active material pack density 1.3 g/cm of a negative electrode, contact into a carbon fiber ingredient (A) and a carbonaceous ingredient becomes good, the network between carbon materials becomes good, and the utilization factor of an electrode improves. Moreover, the binding property between active materials improves. Moreover, when an active material is charge-collector-hard and full, the adhesive property of a charge collector and an active material layer improves. Furthermore, the flexibility of an electrode also improves.
[0033]
[Embodiment of the Invention] Hereafter, the nonaqueous electrolyte rechargeable battery (for example, cylindrical nonaqueous electrolyte rechargeable battery) concerning this invention is explained with reference to drawing 1 .
[0034] For example, as for the container 1 of the shape of a closed-end cylinder which consists of mild steel, the insulator 2 is arranged at the pars basilaris ossis occipitalis. The electrode group 3 is contained in said container 1. Said electrode group 3 has structure which wound around the curled form the band-like object which carried out the laminating of a positive electrode 4, a separator 5, and the negative electrode 6 in this sequence so that said negative electrode 6 might be located outside. Said separator 5 is formed from a nonwoven fabric, a polypropylene fine porosity film, a polyethylene fine porosity film, and a polyethylene-polypropylene fine porosity laminated film.
[0035] The electrolytic solution is held in said container 1. Caulking immobilization of the positive-electrode terminal 9 of the hat configuration arranged at the relief valve 8 arranged under the PTC component 7 by which opening of the hole was carried out to the center section, and said PTC component 7, and said relief valve 8 is carried out through the insulating gasket 10 at up opening of said container 1. In addition, opening of the deflation hole (not shown) is carried out to said positive-

electrode terminal 9. Positive-electrode Read's 11 end is connected to said positive electrode 4, and the other end is connected to said positive-electrode terminal 9, respectively. Said negative electrode 6 is connected to said container 1 which is a negative-electrode terminal through negative-electrode Read who does not illustrate.

[0036] Next, said positive electrode 4, said negative electrode 6, and the electrolytic solution are explained concretely.

[0037] a) Produce the positive-electrode 4 aforementioned positive electrode 4 by judging in the magnitude which asks for what applied to a bigger area than the magnitude for which it asks to one side or both sides to a charge collector by turns for the die length for which it continues or asks, and an uncoated portion, dried and made the positive-electrode material paste which a suitable solvent is made to distribute positive active material, an electric conduction agent, and a binder, and is obtained the shape of sheet metal.

[0038] A lithium compound metallic oxide can be used as said positive active material. As the . aforementioned binder with which LiCoO2, LiNiO2, LiMnO2, LiMn 2O4, etc. are specifically used, that to which the copolymer of the monomer and vinylidene fluoride of the copolymer of polyvinylidene fluoride and vinylidene fluoride-6 propylene fluoride, the 3 yuan copolymer of polyvinylidene fluoride-tetrafluoroethylene-6 propylene fluoride, the copolymer of vinylidene fluoride-pentafluoropropylene, the copolymer of vinylidene fluoride-chlorotrifluoroethylene, or other fluorine systems was carried out can be mentioned. As a copolymer of the starting other fluorine system monomers and vinylidene fluoride The copolymer of tetrafluoroethylene-vinylidene fluoride, the 3 yuan copolymer of tetrafluoroethylene-perfluoroalkyl vinyl ether (PFA)-vinylidene fluoride, To tetrafluoroethylene -, the 3 yuan copolymer of KISAFURUORO propylene (FEP)-vinylidene fluoride, The copolymer of tetrafluoroethylene-ethylene-vinylidene fluoride, The copolymer of chlorotrifluoroethylene-vinylidene fluoride, the 3 yuan copolymer of chlorotrifluoroethylene-ethylene-vinylidene fluoride, and the copolymer of vinyl fluoride-vinylidene fluoride can be mentioned. These may be independently used for said binder.

[0039] As an organic solvent for distributing said binder, N-methyl pyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide, a methyl ethyl ketone, a tetrahydrofuran, an acetone, ethyl acetate, etc. are used.

[0040] As said electric conduction agent, acetylene black, KETCHIEN black, graphite, etc. can be mentioned, for example.

[0041] As for the loadings of said binder, it is desirable to make said active material and said binder into 2 % of the weight - 8% of the weight of the range to the 100 in all weight section (for an electric conduction agent to be also the 100 in all weight section, when said electric conduction agent is included).

[0042] As for the loadings of said electric conduction agent, it is desirable to make it 1 % of the weight - 15% of the weight of the range to said active material 100 weight section.

[0043] As for the loadings of said organic solvent, it is desirable to make said active material and said binder into 65 % of the weight - 150% of the weight of the range to the 100 in all weight section (for an electric conduction agent to be also the 100 in all weight section, when said electric conduction agent is included).

[0044] As the above-mentioned distributed equipment, a ball mill, a bead mill, a dissolver, a Sand grinder, a roll mill, etc. are adopted.

[0045] As said charge collector, aluminium foil with a thickness of 10-40 micrometers, a stainless steel foil, a titanium foil, etc. can be mentioned, for example.

[0046] b) Negative electrode 6 (said negative electrode 6 consists a lithium ion of a thing, a light metal, etc. containing occlusion, the carbonaceous object to emit, or a chalcogen compound.) Especially, in order that cell properties of the negative electrode containing occlusion, the carbonaceous object to emit, or a chalcogen compound, such as a cycle life of said rechargeable battery, may improve a lithium ion, it is desirable.

[0047] Said lithium ion can be mentioned, for example for the baking object of corks, a carbon fiber, a pyrolysis gaseous-phase carbon object, a graphite, a resin baking object, a mesophase pitch based carbon

fiber, or mesophase spherical carbon etc. as occlusion and a carbonaceous object to emit. Especially, since electrode capacitance will become high if the mesophase pitch based carbon fiber graphitized above 2500 degrees C is used, it is desirable. Said lithium ion can be mentioned for 2 titanium sulfides (TiS2), molybdenum disulfide (MoS2), selenium-ized niobium (NbSe2), etc. as occlusion and a chalcogen compound to emit. If such a chalcogen compound is used for a negative electrode, although it descends, since the capacity of said negative electrode increases, the capacity of the electrical potential difference of said rechargeable battery of said rechargeable battery will improve. Furthermore, since said negative electrode has the large diffusion rate of a lithium ion, its quick-charge/discharge-capability ability of said rechargeable battery improves.

[0048] As said light metal, aluminum, an aluminium alloy, a Magnesium alloy, a lithium metal, a lithium alloy, etc. can be mentioned.

[0049] Said negative electrode (for example, negative electrode which consists of carbon material) is produced by judging in the magnitude which asks for what applied to a bigger area than the magnitude for which it asks to one side or both sides to a charge collector by turns for the die length for which it continues or asks, and an uncoated portion, dried and specifically made the negative-electrode material paste which a suitable solvent is made to distribute said carbon material, an electric conduction agent, and a binder, and is obtained the shape of sheet metal.

[0050] As for the blending ratio of coal of said negative-electrode ingredient and a binder, it is desirable that it is the range of 80 - 98 % of the weight of negative-electrode ingredients and 2 - 20 % of the weight of binders. As for said especially carbon material, it is desirable to make it the range of 50 - 200 g/m2 as coverage per one side, where a negative electrode 6 is produced.

[0051] As said charge collector, although copper foil, a nickel foil, etc. can be used, for example, when electrochemical stability, the flexibility at the time of winding, etc. are taken into consideration, copper foil is the most desirable. As thickness of the foil at this time, it is desirable that it is [8 micrometer or more] 20 micrometers or less.

[0052] c) The electrolytic-solution aforementioned electrolytic solution has the presentation which dissolved the electrolyte in the non-aqueous solvent.

[0053] As said non-aqueous solvent, for example Annular carbonate, such as propylene carbonate (PC) and ethylene carbonate (EC), For example, dimethyl carbonate (DMC), methylethyl carbonate (MEC), Chain-like carbonate, such as diethyl carbonate (DEC), 1, 2-dimethoxyethane (DME), Cyclic ether and crown ether, such as diethoxy ethane (DEE), [, such as the chain-like ether, a tetrahydrofuran (THF), and 2-methyl tetrahydrofuran (2-MeTHF)] At least one sort chosen from sulfur compounds, such as nitrides, such as fatty acid ester, such as gamma-butyrolactone (gamma-BL), and an acetonitrile (AN), a sulfolane (SL), and dimethyl sulfoxide (DMSO), etc. can be used.

[0054] It is desirable to use the mixed solvent which consists of at least one sort chosen from what consists of at least one sort chosen from EC, PC, and gamma-BL especially, EC and PC, and gamma-BL, and at least one sort chosen from DMC, MEC, DEC, DME, DEE, THF, 2-MeTHF, and AN. Moreover, when using what contains occlusion and the carbonaceous object to emit in a negative electrode for said lithium ion, it is desirable to use the mixed solvent which consists of EC, PC, gamma-BL and EC, PC, MEC and EC, PC, DEC and EC, PC, DEE and EC, AN, EC and MEC, PC, DMC, PC and DEC, or EC and DEC from a viewpoint which raises the cycle life of the rechargeable battery equipped with said negative electrode.

[0055] As said electrolyte, lithium salt, such as lithium perchlorate (LiClO4), a 6 fluoride [phosphoric-acid] lithium (LiPF6), hoe lithium fluoride (LiBF4), a 6 fluoride arsenic lithium (LiAsF6), a trifluoro meta-sulfonic-acid lithium (LiCF3SO3), an aluminum tetrachloride lithium (LiAlCl4), and a bis-trifluoromethylsulfonyl imide lithium [LiN (CF3SO2)2], can be mentioned, for example. When LiPF6, LiBF4, and LiN (CF3SO2)2 are used especially, it is desirable in order that conductivity and safety may improve.

[0056] As for the amount of dissolutions to said non-aqueous solvent of said electrolyte, it is desirable to make it the range of 0.5 mols / L-2.0 mols / L.

[0057] According to the nonaqueous electrolyte rechargeable battery built over this invention above as

explanation, in a negative electrode, the lithium secondary battery which was excellent also in the adhesion of a charge collector and an active material layer, and was excellent in the cycle-life property can be obtained by using the binder which consists of said acrylic gum copolymer.

(Example) Below, a table 1, a table 2, and a table 3 explain the example of this invention concretely.

[A table 1]

	改良機能材料(A)(重量%比率)	改良買材料(B)(重量%比率)	アクリル系ゴム質共重合体(重量%比率)	ポリフッ化ビニリデン(重量%比率)	充填密度(g/cm3)
実施例1	90	10	3	0	1.4
実施例2	90	10	4	0	1.4
実施例3	90	10	3	0	1.4
実施例4	90	10	3	0	1.4
実施例5	90	10	3	1	1.4
実施例6	90	10	3	2	1.4
実施例7	80	20	4	0	1.4
実施例8	60	40	4	0	1.4
実施例9	80	20	3	1	1.4
実施例10	60	40	3	1	1.4
実施例11	90	10	3	1	1.4
実施例12	90	10	3	0	1.6
実施例13	90	10	3	1	1.6
比較例1	90	10	0	3	1.4
比較例2	90	10	0	5	1.4
比較例3	90	10	0	3	1.4
比較例4	90	10	2	3	1.4
比較例5	90	10	2	4	1.4
比較例6	40	60	4	0	1.4
比較例7	20	80	4	0	1.4
比較例8	40	60	3	1	1.4
比較例9	20	80	3	1	1.4
比較例10	90	10	3	0	1.2
比較例11	90	10	3	1	1.2

[A table 2]

	剥離強度(gf/2cm)
実施例1	46
実施例2	47
実施例3	40
実施例4	47
実施例5	48
実施例6	52
実施例7	40
実施例8	36
実施例9	44
実施例10	38
実施例11	50
実施例12	40
実施例13	42
比較例1	6
比較例2	8
比較例3	12
比較例4	15
比較例5	12
比較例6	13
比較例7	10
比較例8	14
比較例9	15
比較例10	22
比較例11	20

[A table 3]

	500サイクル後 容量維持率(%)
実施例1	86
実施例2	88
実施例3	84
実施例4	88
実施例5	89
実施例6	91
実施例7	84
実施例8	82
実施例9	85
実施例10	83
実施例11	90
実施例12	83
実施例13	84
比較例1	52
比較例2	55
比較例3	58
比較例4	61
比較例5	58
比較例6	59
比較例7	56
比較例8	60
比較例9	61
比較例10	66
比較例11	65

The mixture which mixed and obtained the example 1LiCoO2 powder 100 weight section, and the amount section of acetylene black 2 of 50nm of mean diameters and the phosphorus flaky graphite (artificial graphite) 3 weight section of 1 micrometer of mean diameters with the mixer . which N-methyl pyrrolidone was made to distribute the mixture which consists of the polyvinylidene fluoride 5 weight section which is a binder, and produced the positive-electrode paste, then this were applied to both sides of the aluminium foil as a charge collector, and the positive electrode which rolls out and takes for an example 1 after desiccation was produced.

[0058] The mesophase pitch based carbon fiber was manufactured by on the other hand graphitizing the mesophase pitch carbon fiber which used the mesophase pitch as the raw material.

[0059] After having continued, making N-methyl pyrrolidone distribute the mixture which consists of the acrylic copolymer 3 weight section to the mesophase pitch based carbon fiber 90 weight section to the natural-graphite 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, and after desiccation, the roll press was performed and the negative electrode of pack density 1.4 g/cm3 was produced.

[0060] After carrying out the laminating of the separator which consists of said positive electrode and a porosity film made from polyethylene, and said negative electrode in this sequence, respectively, it wound around the curled form and the electrode group was produced so that said negative electrode might be located outside.
[0061] As the electrolytic solution, what dissolved the 6 fluoride [phosphoric-acid] lithium (LiPF6) in the mixed solvent (mixed volume ratio 1:2) of ethylene carbonate (EC) and methylethyl carbonate (MEC) 1M was used, said electrode group and said electrolytic solution were contained in the closed-end cylindrical cup made from stainless steel, respectively, and the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled.
[0062] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 4 weight section to the natural-graphite 10 weight section and the carbon material powder 100 weight section to the . mesophase pitch based carbon fiber 90 weight section using the same positive electrode as what was used in the example 2 example 1 and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0063] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0064] The same positive electrode as what was used in the example 3 example 1 was used.
[0065] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section to the mesophase pitch based carbon fiber 90 weight section to the corks 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and pack density produced the negative electrode of 1.4 g/cm3.
[0066] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0067] The same positive electrode as what was used in the example 4 example 1 was used.
[0068] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic copolymer 3 weight section to the mesophase pitch based carbon fiber 80 weight section to the natural-graphite 20 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0069] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0070] The same positive electrode as what was used in the example 5 example 1 was used.
[0071] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section and the polyvinylidene fluoride 1 weight section to the mesophase pitch based carbon fiber 90 weight section to the artificial ****** 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0072] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0073] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section and the polyvinylidene fluoride 2 weight section to the artificial ****** 10 weight section and the carbon material powder 100 weight section to the . mesophase pitch based carbon fiber 90 weight section using the same positive electrode as what was used in the example 6 example 1 and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack-density 1.4 g/cm3 was produced.
[0074] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.

[0075] The same positive electrode as what was used in the example 7 example 1 was used.
[0076] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 4 weight section to the mesophase pitch based carbon fiber 80 weight section to the artificial ****** 20 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0077] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0078] The same positive electrode as what was used in the example 8 example 1 was used.
[0079] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 4 weight section to the mesophase pitch based carbon fiber 60 weight section to the artificial ****** 40 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0080] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0081] The same positive electrode as what was used in the example 9 example 1 was used.
[0082] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section and the polyvinylidene fluoride 1 weight section to the mesophase pitch based carbon fiber 80 weight section to the artificial ****** 20 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0083] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0084] The same positive electrode as what was used in the example 10 example 1 was used.
[0085] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section and the polyvinylidene fluoride 1 weight section to the mesophase pitch based carbon fiber 60 weight section to the artificial ****** 40 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0086] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0087] As opposed to the example 11 mesophase pitch based carbon fiber 90 weight section The artificial ****** 10 weight section, Two fluorines, the acrylic gum copolymer 3 weight section and vinylidene fluoride, are permuted by the carboxyl group to the carbon material powder 100 weight section, respectively. After making N-methyl pyrrolidone distribute the mixture which consists of the denaturation polyvinylidene fluoride 1 weight section to which the polymerization of the 1 % of the weight of the monomers used as the anhydride was carried out with vinylidene fluoride and making it the shape of a paste, It applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0088] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0089] The same positive electrode as what was used in the example 12 example 1 was used.
[0090] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic copolymer 3 weight section to the mesophase pitch based carbon fiber 90 weight section to the natural-graphite 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, and after desiccation, the roll press was performed and the negative electrode of pack density 1.6 g/cm3 was

produced.
[0091] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0092] The same positive electrode as what was used in the example 13 example 1 was used.
[0093] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section and the polyvinylidene fluoride 1 weight section to the mesophase pitch based carbon fiber 90 weight section to the artificial ****** 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.6 g/cm3 was produced.
[0094] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1. Negative-electrode pack density is 1.6 g/cm3.
[0095] The same positive electrode as what was used in the example of comparison 1 example 1 was used.
[0096] After making N-methyl pyrrolidone distribute the mixture which consists of the polyvinylidene fluoride 3 weight section to the mesophase pitch based carbon fiber 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0097] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0098] The same positive electrode as what was used in the example of comparison 2 example 1 was used.
[0099] After making N-methyl pyrrolidone distribute the mixture which consists of the polyvinylidene fluoride 5 weight section to the mesophase pitch based carbon fiber 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0100] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1. Negative-electrode pack density is 1.4 g/cm3.
[0101] The same positive electrode as what was used in the example of comparison 3 example 1 was used.
[0102] After making N-methyl pyrrolidone distribute the mixture which consists of the 3 weight sections of the denaturation polyvinylidene fluoride to which the polymerization of the 1 % of the weight of the monomers which permuted two fluorines of the vinylidene fluoride which is a binder by the carboxyl group, respectively, and were used as the anhydride was carried out with vinylidene fluoride to the mesophase pitch based carbon fiber 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of 3 be produced 1.4g [/cm] pack density.
[0103] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0104] The same positive electrode as what was used in the example of comparison 4 example 1 was used.
[0105] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 2 weight section and the polyvinylidene fluoride 3 weight section to the mesophase pitch based carbon fiber 90 weight section to the artificial ****** 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of 3 was produced 1.4g [/cm] pack density.
[0106] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.

[0107] The same positive electrode as what was used in the example of comparison 5 example 1 was used.
[0108] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 2 weight section and the polyvinylidene fluoride 4 weight section to the mesophase pitch based carbon fiber 90 weight section to the artificial ****** 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of 3 was produced 1.4g [/cm] pack density.
[0109] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0110] The same positive electrode as what was used in the example of comparison 6 example 1 was used.
[0111] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 4 weight section to the mesophase pitch based carbon fiber 40 weight section to the artificial ****** 60 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0112] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0113] The same positive electrode as what was used in the example of comparison 7 example 1 was used.
[0114] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 4 weight section to the mesophase pitch based carbon fiber 20 weight section to the artificial ****** 80 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0115] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0116] The same positive electrode as what was used in the example of comparison 8 example 1 was used.
[0117] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section and the polyvinylidene fluoride 1 weight section to the mesophase pitch based carbon fiber 40 weight section to the artificial ****** 60 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0118] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0119] The same positive electrode as what was used in the example of comparison 9 example 1 was used.
[0120] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section and the polyvinylidene fluoride 1 weight section to the mesophase pitch based carbon fiber 20 weight section to the artificial ****** 80 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.4 g/cm3 was produced.
[0121] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0122] The same positive electrode as what was used in the example of comparison 10 example 1 was used.
[0123] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum

copolymer 4 weight section to the mesophase pitch based carbon fiber 90 weight section to the natural-graphite 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.2 g/cm3 was produced.
[0124] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0125] The same positive electrode as what was used in the example of comparison 11 example 1 was used.
[0126] After making N-methyl pyrrolidone distribute the mixture which consists of the acrylic gum copolymer 3 weight section and the polyvinylidene fluoride 1 weight section to the mesophase pitch based carbon fiber 90 weight section to the natural-graphite 10 weight section and the carbon material powder 100 weight section and making it the shape of a paste, it applied to both sides of the copper foil which is a charge collector substrate, the roll press was performed after desiccation, and the negative electrode of pack density 1.2 g/cm3 was produced.
[0127] Hereafter, the cylindrical shape rechargeable lithium-ion battery (18650 sizes) of design rated capacity 1600mAh was assembled like the example 1.
[0128] First, about each obtained negative electrode, in order to investigate adhesion with a charge collector, the peel strength trial was performed using the hauling testing machine. Cut down each positive electrode of examples 1-13 and the examples 1-11 of a comparison to 2cm width-of-face x5cm length, the spreading side was made to exfoliate at a fixed rate as a test piece while the double-sided tape maintained one [lamination and] edge at the include angle of 180 degrees in the direction of a long side in the glass side, and the reinforcement at that time was measured as adhesion reinforcement. This result is shown in the following table 1.
[0129] Examples 1-13 have checked that adhesion reinforcement was large compared with the examples 1-11 of a comparison which used polyvinylidene fluoride so that more clearly than this table.
[0130] Next, the cycle-life trial was performed about each cell of examples 1-13 and the examples 1-11 of a comparison. After carrying out to 4.2V by 800mA of charging currents in 20 degrees C, charge was held by the constant voltage of 4.2V, and was performed for a total of 5 hours. Discharge was performed by 800mA constant current, and discharge final voltage was set to 2.7V. The quiescent time after charge and discharge was made into 30 minutes, respectively. It carried out by having repeated such charge and discharge, and discharge capacity was measured for every cycle. And the capacity maintenance factor to the discharge capacity of 1 cycle eye of the discharge capacity of a 500 cycle eye is shown in a table 2.
[0131] As shown in a table 2, it turns out that each cycle life shows 80% or more of capacity maintenance factors in 500 cycles, and the lithium secondary battery of examples 1-13 using the acrylic copolymer as a binder is excellent in a charge-and-discharge cycle property.
[0132] On the other hand, the lithium secondary battery of the examples 1-11 of a comparison has checked that a cycle life was short compared with examples 1-13.
[0133] In addition, in the example mentioned above, although the example applied to the cylindrical shape nonaqueous electrolyte rechargeable battery was explained, it is applicable also like the square shape nonaqueous electrolyte rechargeable battery of the structure where a positive electrode, a negative electrode, a separator, and nonaqueous electrolyte were contained in the closed-end rectangle tubed container.
[0134]
[Effect of the Invention] According to the nonaqueous electrolyte rechargeable battery built over this invention above as explanation, in a negative electrode, the nonaqueous electrolyte rechargeable battery which was excellent also in the adhesion of a charge collector and an active material layer, and was excellent in the cycle-life property can be obtained by using the binder which consists of said acrylic gum copolymer.

[Translation done.]